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(19)



Europäisches Patentamt  
European Patent Office  
Office européen des brevets

(11) Publication number:

**0 109 059**  
**A1**

(12)

# EUROPEAN PATENT APPLICATION

(21) Application number: 83111240.4

(51) Int. Cl.<sup>2</sup>: **C 07 C 11/06, C 07 C 4/10,**  
**B 01 J 29/28, B 01 J 29/38**

(22) Date of filing: 10.11.83

(30) Priority: 10.11.82 IT 2415282  
02.12.82 IT 2455082  
27.01.83 IT 1829283  
03.05.83 IT 2089683

(43) Date of publication of application: 23.05.84  
Bulletin 84/21

(84) Designated Contracting States: DE FR GB IT

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(54) **Process for converting olefins having 4 to 12 carbon atoms into propylene.**

(57) A process for converting olefins having from 4 to 12 carbon atoms into propylene, wherein said olefins are contacted with an aluminosilicate having a crystalline and zeolitic structure and having a  $\text{SiO}_2/\text{Al}_2\text{O}_3$  molar ratio equal to or lower than 300, at a space velocity higher than 50 kg/h of olefins per kg of pure zeolite and at a temperature of from 400 to 600°C, whereby said aluminosilicate is preferably selected from zeolites ZSM 5 and ZSM 11, and is used as such or in a modified form.

**EP 0 109 059 A1**

0109059

PROCESS FOR CONVERTING OLEFINS HAVING 4 TO 12 CARBON  
ATOMS INTO PROPYLENE

5 The invention relates to a process for converting olefins having 4 to 12 carbon atoms into propylene.

Nowadays, huge amounts of olefinic cuts from  $C_4^-$  to  $C_{12}^-$ , either linear or branched, are available throughout the world and they are widely employed for different purposes, such as described e.g. in Italian patent publications 24152 A/82, 24550 A/82 and 19292 A/83.

15 Sometimes however, because of contingent reasons even outside the chemical field such as for instance transportation difficulties, it would be better to have still further possibilities of use.

A promising use of said olefins would be their conversion into propylene and/or ethylene.

20 It is an object of the present invention to provide a process for converting olefinic cuts from  $C_4^-$  to  $C_{12}^-$  to propylene with a high yield of propylene and, optionally, also ethylene.

25 In its most general form, the invention relates to a process for converting olefins having 4 to 12 carbon atoms into propylene, which is characterized in that said olefins are brought into contact with an alumino-silicate having a crystalline and zeolitic structure and having a  $SiO_2/Al_2O_3$  molar ratio (Z ratio) equal to or lower than 300, at space velocities higher than 50 kg/h of olefins per kg of pure zeolite and at temperatures of from 400 to 600°C, whereby said alumino-silicate is preferably selected from zeolites ZSM 5 and ZSM 11, and is used as such or in a modified form.

35 Generally, the lower the Z ratio, the higher the space velocity; the examples show very good results correspon-

ding to a Z ratio of 28, but higher ratios are equally or more effective.

5 The catalyst comprises preferably zeolites of the ZSM type, as described e.g. in European patent publication 36707; best results were attained by using ZSM 5 or ZSM 11  
zeolites in their acid form (H - ZSM 5 or H - ZSM 11), or  
in a modified form (for instance by means of phosphorus,  
10 magnesium, calcium, strontium, barium, chromium, copper or zinc).

The modifying element can be incorporated into the catalyst by means of ion exchange or by other methods, for  
15 example impregnation or co-precipitation during the zeolite synthesis.

According to a particularly advantageous way for the preparation of a non-modified catalyst (e.g. H-ZSM 5), the  
20 raw product coming from the zeolite synthesis is dried, for instance at 120°C, calcined (e.g. at 540°C for some hours, in order to displace all the residual templating agent) and then exchanged with an aqueous solution of HCl, NH<sub>4</sub>Cl, NH<sub>4</sub>NO<sub>3</sub> or an equivalent H<sup>+</sup> or NH<sub>4</sub><sup>+</sup> source. When  
25 an ammonium compound is used, it is necessary to heat, for instance at 400°C, in order to obtain the acid form. A survey of alternative techniques for the ion exchange is given e.g. in US patents 3,140,249; 3,140,251; 3,140,253 and in European patent publications 30796, 36707,  
30 37168, 40463 and 68754. The zeolite, after calcination and conversion into the acid form, has a long life and a very high catalytic activity. The zeolites mentioned above can be used as catalysts (as such or in a modified form) optionally in admixture with suitable amounts of oxides  
35 as binders, for instance SiO<sub>2</sub> or Al<sub>2</sub>O<sub>3</sub>. Other binders are disclosed e.g. in European patent publication 36707.

The regeneration of the catalyst can be carried out in air for some hours at 400 - 600°C. A steam regeneration

is described in European patent publication 36704 and according to a further and very successful method, the catalyst can be regenerated by a hydrogen treatment.

As to the initial activation of the catalyst, some methods are described in European patent publications 34444 and 35830; in general, it is advisable to activate the catalyst for some hours in air at 450 - 750°C (preferably at 540 - 700°C).

Any process for the conversion of olefinic cuts to propylene will be indicated hereafter as a "post-pyrolysis" process. When the raw material of a post-pyrolysis process is a mixture of olefins having 4 C atoms, there is a considerable problem to be solved, because the  $C_4^-$  cuts always contain substantial amounts of paraffins in general also having 4 C atoms, which paraffins pass (at 400 - 600°C) the zeolite bed without taking part in any reaction.

Furthermore, a small amount of  $C_4$  paraffins is produced by the post-pyrolysis process itself. The conversion to  $C_3H_6$  could be enhanced by a recycle of the non-reacted  $C_4^-$  olefins or of the  $C_4^-$  olefins formed during the reaction. In such a case however, an increasing accumulation of n-butane and of isobutane would take place. This drawback could be avoided by separating paraffins from olefins before feeding the reactor, but such a separation is rather difficult. Butenes and isobutane cannot be isolated by a simple distillation and it is usually necessary to carry out an extractive distillation (a troublesome technique) which is particularly difficult for the  $C_4^-$  cuts coming from catalytic cracking, where butane and isobutane may account for up to 50% of the whole. The problem however can be solved in a surprisingly easy way by the process according to the invention, when employing an integrated oligomerization step. In other words, a particular embodiment of the invention (the feed being a paraffin-olefin mixture) comprises the following steps (reference is made

also to figure 1):

- 5 a) a preliminary oligomerization of a ( $C_4^- + C_4^+$ ) mixture at a temperature of from 320 to 380°C, using a catalyst bed of zeolitic nature (see e.g. US patent No. 4,150,062) to obtain a mixture of olefins having from 5 to 8 C atoms, the  $C_4^+$  paraffins remaining substantially unconverted;
- 10 b) cooling and condensation of the oligomerization effluent in order to separate the  $C_4^+$  paraffins as a gaseous phase, and conversion of the remaining ( $C_5^- - C_8^-$ ) mixture to propylene under the typical post-pyrolysis reaction conditions described above;
- 15 c) cooling the effluent from the reactor for the conversion to propylene and compression of said effluent, preferably at 13 - 16 absolute kg/cm<sup>2</sup>, whereby the hydrocarbons having 4 or more C atoms are condensed and the hydrocarbons having less than 4 C atoms are  
20 separated as a gaseous phase.

These hydrocarbons ( $< C_4$ ) can be advantageously fed to a conventional battery of distillation columns for thermal or catalytic cracking in order to recover all the propylene contained therein. The small amounts of aromatics (BTX) can be easily separated from the other  $\geq C_4$  hydrocarbons, if necessary, and recycled together with the final ( $C_4^- - C_8^-$ ) mixture, containing small amounts of butanes, produced during the conversion reaction described under  
25 item (b) above. In order to carry out the oligomerization,  $C_4^-$  olefins containing  $C_4^+$  paraffins in any proportion, are initially brought into contact with a catalyst of zeolitic nature, for instance ZSM 5 or ZSM 11, in an acid or in a modified form, at 250 - 400°C (preferably 320 - 380°C)  
30 and at space velocities from 2 to 10 (preferably 4 - 8) kg/h of reactants per kg of pure zeolite (binder excluded). In other words, the olefins of the ( $C_4^- + C_4^+$ ) mixture are converted almost totally into a ( $C_5^- - C_8^-$ ) olefinic mixture, while butane and isobutane do not react. The

separation of the butanes can thus be carried out very easily by simple cooling with water at room temperature. The olefinic ( $C_5^- - C_8^-$ ) mixture liquifies while the butanes are separated as a gaseous phase, said ( $C_5^- - C_8^-$ ) mixtures being optimal raw materials for the production of propylene. Depending on the working conditions during the synthesis of the zeolite, such as e.g. the dilution of the starting solutions, the zeolite crystallites may have a widely variable size; in general, a sharp subdivision is noted at  $0.5 - 1 \mu m$ , i.e. the crystallites' dimensions are generally above that level ("large size" crystals) or below that level ("small size" crystals). The catalysts according to the present invention are preferably "small size" crystals and can e.g. be prepared according to the methods of US patent No. 3,926,782.

The following examples are given merely for illustrative purposes and do not in any way limit the scope of the invention.

#### Working conditions common to all the examples

- a) Zeolite ZSM 5 was prepared according to example 24 of US patent 3,702,886 with stirring, so as to obtain crystallites having an average size below  $0.5 \mu m$ ;
- b) zeolite ZSM 11 was prepared according to US patent 3,709,979 with stirring, so as to obtain crystallites having an average size below  $0.5 \mu m$ ;
- c) the modified zeolites were obtained by ion exchange, unless otherwise specified in the tables;
- d) all the catalysts were activated prior to use at  $540^\circ C$  for 2 hours, unless otherwise specified in the tables.

#### Examples 1 to 20

The zeolites, mixed with  $SiO_2$  as a binder, were charged into a microreactor which was continuously fed at a pressure slightly higher than atmospheric pressure with a

mixture consisting of equal proportions (1:1) of 2-cis-butene and 2-trans-butene. The reaction conditions and results are given in table 1.

#### Example 21 (Regeneration Test)

After an 18-hour run according to example 20, the reaction was stopped and the catalyst was regenerated with air, at atmospheric pressure and at the reaction temperature (550°C) for 2 hours; feeding of butenes was started again according to the conditions of example 25 and after 1 hour the following results were obtained:

15	Conversion	88.60%
	Selectivity to iso $C_4^-$	8.62%
	Selectivity to $C_3^-$	38.50%
	Yield of iso $C_4^- + C_3^-$	41.75%
	Selectivity to $\geq C_5$	33.54%
20	Selectivity to saturated gases $\leq C_4$	11.97%
	Selectivity to $C_2^-$	7.37%

#### Examples 22 to 44

25 0.5 g of zeolite, mixed with 0.21 g of  $Al_2O_3$  as a binder, were charged into a microreactor which was continuously fed, at a pressure slightly higher than atmospheric pressure with an 0.7:1 (by moles) mixture of n-pentene-1 and helium. The reaction conditions and results are given in table 2.

#### Examples 45 to 48

35 These examples were carried out according to the preceding examples, but pentene was substituted by n-hexene (examples 45 to 46) and n-octene-1 (examples 47 and 48), respectively. Data and results are given in table 3.



Examples 49 and 50

These examples were carried out according to examples 22 to 44, but pentene was substituted by an olefin fraction  $C_5$ , coming from a fluid bed catalytic cracking (FCC) and essentially consisting of hydrocarbons having 5 carbon atoms with approximately the following composition:

Olefins ( $C_5^-$ ) = 70% by weight;

Paraffins ( $C_5^+$ ) = 30% by weight;

Dienes  $\leq 0.5$  by weight.

Data and results are given in table 3.

Examples 51 and 52

Examples 45 and 46 were repeated, substituting linear hexene by a branched isomer (2-methyl-1-pentene). Data and results are given in table 3.

It is apparent from the above that the cracking of branched olefins according to the present invention substantially leads to the same results as the cracking of the corresponding linear olefins. This is surprising in so far as it was believed until now (see European patent publication 37,671) that linear olefins were far easier to convert in the presence of zeolites than the branched isomers.

Examples 53 to 60

3 g of H - ZSM 5 mixed with 0.9 g of  $SiO_2$  as a binder, were loaded into a microreactor which was continuously fed with isobutene, at a pressure slightly higher than atmospheric pressure. Reaction conditions and results are given in table 4.

These tests show the influence of the temperature on the reaction.

Examples 61 to 68

5 These tests were carried out by repeating example 55  
(at 550°C) and varying the space velocity, i.e. the resi-  
dence time. In this way it was possible to ascertain  
that for velocities up to about  $311 \text{ h}^{-1}$ , the increase  
in selectivity to  $\text{C}_3^-$  compensates at least partially the  
10 decrease suffered by the conversion in the long run. Data  
and results are indicated in table 4.

Examples 69 and 70

15 These tests were carried out by repeating example 65 and  
raising the temperature to 580°C. Data and the excellent  
results are indicated in table 4.

Examples 71 and 72

20 These tests were carried out by repeating example 55, em-  
ploying a zeolite H - ZSM 5 with a much higher  $\text{SiO}_2/\text{Al}_2\text{O}_3$   
molar ratio (204). The data and results given in table 4  
show that the propylene yield was positively influenced  
by the increase in said ratio. However, if such ration  
25 increases excessively, a drastic reduction in the  $\text{C}_3^-$   
yield occurs at higher space velocities.

Examples 73 and 74

30 These tests were performed by repeating example 57 and  
employing a zeolite activated for 2 hours at a higher  
temperature i.e. at 700°C; the reaction data are indi-  
cated in table 4 together with the excellent results  
which prove the positive influence exerted by the in-  
35 crease in the catalyst activation temperature.

Examples 75 and 76

These tests were carried out by repeating example 57 and

substituting the zeolite in the acid form by a zeolite partially exchange with Cr; the exchanged zeolite contained  
5 0.8% by weight of Cr. Data and results are in table 4.

#### Examples 77 to 79

These tests were performed by repeating example 57 and substituting the zeolite in the acid form by a zeolite exchanged  
10 with Mg. The tests prove that a modification with Mg exhibits excellent aspects (see table 4).

#### Examples 80 and 81 (Comparative Tests)

15 These tests were performed by repeating example 55 and reducing the space velocity to a very low value ( $3.5 \text{ h}^{-1}$ ). The low propylene yield clearly proves the importance of a velocity exceeding the critical value ( $50 \text{ h}^{-1}$ ); see table 4.

#### 20 Example 82

##### PART A

As shown in figure 1, a reactor (A) was loaded with 10 g of the H - ZSM 5 of example 1 and was then continuously fed,  
25 at  $2 \text{ kg/cm}^2$  (absolute) and  $350^\circ\text{C}$ , with the 50/50 butenes mixture of example 1, the space velocity being  $12.5 \text{ kg/h}$  of butenes per kg of H - ZSM 5; the gaseous products were cooled and condensed (at  $15^\circ\text{C}$ ), thus obtaining  $61.1 \text{ g/h}$  of liquids and  $63.9 \text{ g/h}$  of gas. The gases contained  $95.6 \%$   
30 by weight of isobutane, the rest being light olefins and paraffins ( $\leq \text{C}_4$ ) and the liquids contained  $99\%$  by weight of a ( $\text{C}_5^- - \text{C}_8^-$ ) mixture, the rest being aromatics.

##### 35 PART B

The liquids obtained according to PART A were fed continuously to a second reactor (D) at  $550^\circ\text{C}$  and atmospheric pressure, the space velocity being  $\text{WHSV} = 65 \text{ h}^{-1}$ ; said reactor had been loaded with  $3.3 \text{ g}$  of the same H - ZSM 5 of PART A. After a 4-hour run, the effluent from reactor (D)

had the following composition (% by weight):

5	$C_2^+$	0,39	iso- $C_4^-$	8,50	BTX
	$C_2^-$	4,87	$C_5^- + C_6^-$	18,53	
	$C_3^+$	6,44	Benzene	1,06	
	$C_3^-$	31,88	Toluene	5,28	
	$C_4^+$	4,06	Xylenes	6,16	
10	n- $C_4^-$	12,83			

Said effluent was used for the pre-heating of the feed stream (of reactor D) and was then compressed by (E) and cooled with condenser (F), resulting in:

- 15 a) a gaseous stream, rich in propylene, which can be rectified in (G), so as to recover  $C_3^-$  and, optionally also  $C_2^-$ ;
- 20 b) a liquid stream, which can also be rectified - in (H) - so as to separate, if necessary, the very small amount of aromatics.

### Example 83

25 PART B of example 82 was repeated, increasing the space velocity to  $128 \text{ h}^{-1}$ ; after a 4-hour run the effluent from (D) had the following composition (% by weight):

30	$C_2^+$	0,34	iso- $C_4^-$	7,39	BTX
	$C_2^-$	5,54	$C_5^- + C_6^-$	25,85	
	$C_3^+$	5,15	Benzene	1,03	
	$C_3^-$	32,37	Toluene	4,72	
	$C_4^+$	2,99	Xylenes	5,12	
35	n- $C_4^-$	9,50			

TABLE 1

EXAMPLE	1	2	3	4	5	6	7
<b>Operative conditions:</b>							
Catalyst	H-ZSM5(b)		See ex. 1	H-ZSM5	See ex. 4	H-ZSM11	See ex. 6
SiO <sub>2</sub> /Al <sub>2</sub> O <sub>3</sub> (moles)	28	"	"	28	"	82	"
Amount of catalyst	(c) 500	"	"	3 grams (d) 400	"	see ex. 4 500	"
Temp. (°C)	60	"	"	60	550	60	"
Space velocity (a)	6 h	215 6 h	427 6 h	6 h	6 h	1 h	6 h
Data survey after:							
<b>Results (x.b.w.)</b>							
Conversion	88.58	80.05	74.55	91.11	87.84	88.45	86.03
Selectivity to iso-C <sub>4</sub> <sup>-</sup>	9.28	15.26	17.37	7.58	9.39	9.46	11.60
Selectivity to C <sub>2</sub> <sup>-</sup>	31.99	34.32	34.37	16.74	40.65	33.10	35.03
Yield (iso C <sub>4</sub> <sup>-</sup> + C <sub>3</sub> <sup>-</sup> )	36.56	39.69	38.57	21.25	43.86	37.64	40.12
Sel. to compounds C <sub>2</sub> <sup>-</sup> to C <sub>5</sub> <sup>-</sup>	41.31	42.60	42.22	69.15	31.80	41.10	41.55
Sel. to saturated Compounds C <sub>4</sub> <sup>-</sup> to C <sub>6</sub> <sup>-</sup>	13.19	5.64	4.32	5.52	10.80	11.95	8.09
Selectivity to C <sub>2</sub> <sup>-</sup>	4.22	2.28	1.73	1.02	7.37	4.39	3.73

(a) MHSV (Weight Hourly Space Velocity) namely Kg/h of olefines per Kg. of pure zeolite (binder excluded);

(b) 30% b.w. SiO<sub>2</sub> (binder);

(c) depending on pre-fixed MHSV;

(d) 3 g of zeolite + 0.9 g of SiO<sub>2</sub>.

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TABLE 1 (Continuation)

EXAMPLE	8	9	10	11	12	13
<u>Operative conditions:</u>						
Catalyst	H-ZSM5	See ex 8	H-ZSM5	H-P-ZSM5	H-ZSM5	See ex.12
SiO <sub>2</sub> /Al <sub>2</sub> O <sub>3</sub> (mole)	204	"	28	see ex.10	28	"
Amount of catalyst	see ex.4	"	see ex.4	"	see ex.4	"
Temp... (°C)	550	"	500	"	550	"
Space velocity (a)	60	"	60	"	82	"
Data survey after:	1 h	6 h	1 h	"	1 h	6 h
<u>Results (a.b.v.)</u>						
Conversion	88.02	84.26	93.11	80.97	86.42	83.33
Selectivity to iso-C <sub>4</sub>	9.13	12.52	5.44	14.97	10.41	13.02
Selectivity to C <sub>3</sub>	37.98	38.01	28.14	36.88	44.36	45.72
Yield (iso C <sub>4</sub> + C <sub>3</sub> )	41.55	42.50	31.27	41.82	47.33	49.00
Sel. to compounds C <sub>5</sub>	35.77	39.32	40.54	40.48	27.48	27.87
Sel. to saturated						
Compounds C <sub>4</sub>	10.36	5.54	21.34	5.22	10.34	7.49
Selectivity to C <sub>2</sub>	6.75	4.71	4.54	2.66	7.41	5.85

(a) WHSV (Weight Hourly Space Velocity) namely Kg/h of olefines per Kg. of pure zeolite (binder excluded);

(\*) Zeolite H-P-ZSM5 was containing 3.17 b.v. of phosphorus; trimethyl-phosphite was added according to Vedrine et. al. "J. Catal. 73, 147 (1982).

(\*\*) Zeolite H-ZSM5 was activated 2 h at 700°C in air, before being used.

TABLE 1 (Continuation)

EXAMPLE	14	15	16	17	18	19	20
Operative conditions:							
Catalyst	Zn-ZSM5	Cr-ZSM5	See ex. 15	Cu-ZSM5	See ex. 17	See ex. 17	See ex. 19
SiO <sub>2</sub> /Al <sub>2</sub> O <sub>3</sub> (moles)	28	See ex. 14	"	See ex. 14	"	"	"
Amount of catalyst	See ex. 4	"	"	"	"	"	"
Temp... (°C)	550	"	"	"	"	"	"
Space velocity (a)	50	"	"	"	"	83	"
Data survey after:	6 h	1 h	6 h	1 h	6 h	1 h	6 h
Results (xh.w.)							
Conversion	90.67	89.86	88.27	93.66	80.99	88.62	79.30
Selectivity to iso-C <sub>4</sub>	6.88	7.50	8.88	4.45	15.56	8.74	16.86
Selectivity to C <sub>4</sub> <sup>-</sup>	32.10	37.34	38.57	26.48	43.42	38.83	42.13
Yield (iso C <sub>4</sub> <sup>-</sup> + C <sub>3</sub> <sup>-</sup> )	35.34	40.29	41.88	28.97	47.77	42.12	46.78
Sel. to compounds C <sub>4</sub> <sup>-</sup> + C <sub>3</sub> <sup>-</sup>	46.62	34.39	35.81	47.94	28.73	34.70	30.41
Sel. to saturated compounds C <sub>4</sub> <sup>-</sup>	8.49	12.81	9.47	14.35	7.09	10.35	5.79
Selectivity to C <sub>2</sub> <sup>-</sup>	5.92	7.97	7.26	6.79	5.19	7.40	4.31

(a) WHSV (Weight Hourly Space Velocity) namely Kg/h of olefines per Kg. of pure zeolite (binder excluded);

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TABLE 2

EXAMPLE	22	23	24	25	26	27	28	29
<u>Operative Conditions:</u>								
Catalyst	H-ZSM5	H-ZSM5	See ex. 23	See ex. 23	See ex. 25	See ex. 23	See ex. 27	See ex. 23
SiO <sub>2</sub> /Al <sub>2</sub> O <sub>3</sub> (moles)	28	28	"	"	"	"	"	"
Amount of catalyst	(c)	(c)	"	"	"	"	"	"
Temp. (°C)	400	500	"	"	"	550	"	585
Space velocity (a)	71.4	71.4	"	142.8	"	71.4	"	178.6
Data survey after:	1 h	1 h	6 h	1 h	6 h	1 h	6 h	7 h
<u>Results (% b.v.)</u>								
Conversion	65.31	82.80	78.92	70.40	62.88	88.98	84.25	82.83
Selectivity to C <sub>2</sub> <sup>-</sup>	4.01	13.50	13.46	12.77	12.45	21.26	21.87	25.32
Selectivity to C <sub>3</sub> <sup>-</sup>	23.30	27.36	33.06	33.71	36.50	30.31	37.50	36.69
Yield (C <sub>2</sub> <sup>-</sup> + C <sub>3</sub> <sup>-</sup> )	17.83	33.75	36.71	32.72	30.78	45.89	45.99	51.36
Sol. to saturated compounds < C <sub>4</sub>	2.94	8.20	5.04	4.33	2.77	6.46	3.11	2.36
Sol. to C <sub>4</sub> <sup>+</sup>	30.84	17.37	23.62	27.44	32.16	13.28	19.54	17.67
Sol. to C <sub>4</sub> <sup>+</sup>	12.00	12.41	8.78	7.36	5.23	6.81	4.01	2.47
Sol. to BTX (b)	10.14	15.84	10.66	9.26	6.10	19.07	11.27	12.83
Sol. to other								
Liquids	17.27	5.20	5.22	5.31	4.90	2.79	2.60	1.93

(a) See ex. 1; (b) BTX = benzene + toluene + xylene; (c) 0.5 g of pure zeolite + 0.21 g of Al<sub>2</sub>O<sub>3</sub> (binder).



T A B L E 2 (Continuation)

EXAMPLE	30	31	32	33	34	35	36
Operative Conditions:	(c)	(c)	(d)	(*)	(*)	(**)	(**)
Catalyst	H-ZSM5	See ex. 30	H-ZSM5	Cr-H-ZSM5	See ex. 33	Zn-ZSM5	See ex. 35
SiO <sub>2</sub> /Al <sub>2</sub> O <sub>3</sub> (moles)	28	"	see ex. 30	see ex. 30	"	26	"
Amount of catalyst	see ex. 23	"	"	"	"	see ex. 23	"
Temp. (°C)	500	"	"	"	"	550	"
Space velocity (a)	55.7	"	"	"	"	71.4	"
Data survey after:	1 h	6 h	6 h	?	5.25 h	1 h	6 h
Results (% b.w.)							
Conversion	81.08	77.69	65.78	77.55	75.89	89.10	81.10
Selectivity to C <sub>2</sub> <sup>-</sup>	12.56	12.71	11.28	12.70	12.49	20.71	21.69
Selectivity to C <sub>3</sub> <sup>-</sup>	28.71	32.85	34.93	32.04	34.77	25.02	29.89
Yield (C <sub>2</sub> <sup>-</sup> + C <sub>3</sub> <sup>-</sup> )	33.46	35.40	30.40	34.70	35.87	40.75	41.83
Sel. to saturated compounds < C <sub>4</sub>	7.44	5.24	3.30	4.80	4.14	1.73	1.01
Sel. to C <sub>4</sub> <sup>+</sup>	19.31	24.86	34.14	25.07	25.77	11.66	15.65
Sel. to C <sub>4</sub> <sup>+</sup>	11.93	9.18	4.74	9.35	7.35	4.20	2.28
Sel. to BTX (b)	13.80	11.08	4.82	12.02	9.75	32.92	23.30
Sel to other							
liquids	6.17	6.39	5.94	6.00	5.73	3.64	2.81

(a) See ex. 1; (b) BTX = benzene + toluene + xylenes; (c) Zeolite H-ZSM5 was activated 2 h at 600°C before being used;

(d) Zeolite H-ZSM5 was activated 2 h at 700°C.

(\*) Chromium was added by means of a partial ion exchange.

(\*\*) Zn was added by means of a complete ion exchange, as to occupy practically all the sites within the Zeolite.

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T A B L E 2 (Continuation)

EXAMPLE	37	38	39	40	41	42	43	44
<b>Operative Conditions:</b>								
Catalyst	Cr-ZSM5	See ex. 37	Cu-ZSM5	See ex. 39	H-ZSM 11	Na-H-ZSM11	H-ZSM 5	P-H-ZSM 5
SiO <sub>2</sub> /Al <sub>2</sub> O <sub>3</sub> (moles)	See ex. 35	"	See ex. 35	"	80	See ex. 41	208	28
Amount of catalyst	"	"	"	"	See ex. 23	"	See ex. 41	See ex. 41
Temp. (°C)	"	"	"	"	550	"	"	"
Space velocity (a)	"	"	"	"	71.4	"	"	"
Data survey after:	1 h	6 h	1 h	6 h	6 h	6 h	6 h	6 h
<b>Results (% b.w.)</b>								
Conversion	84.75	77.96	89.56	78.33	63.84	63.06	49.43	70.56
Selectivity to C <sub>2</sub> <sup>-</sup>	21.85	21.66	20.69	22.42	20.34	20.07	21.02	22.05
Selectivity to C <sub>3</sub> <sup>-</sup>	37.65	38.48	28.06	40.48	40.22	40.27	41.29	38.36
Yield (C <sub>2</sub> <sup>-</sup> + C <sub>3</sub> <sup>-</sup> )	50.43	46.89	43.66	49.27	38.39	38.05	30.80	42.63
Sel. to saturated compounds < C <sub>4</sub>								
Sel. to C <sub>4</sub> <sup>+</sup>	3.47	3.46	4.36	2.48	1.28	0.96	0.77	2.84
Sel. to C <sub>4</sub> <sup>+</sup>	19.89	24.86	13.58	23.82	29.17	30.16	29.96	24.91
Sel. to C <sub>4</sub> <sup>+</sup>	4.01	2.28	4.00	1.90	1.74	1.20	0.89	2.86
Sel. to BTX (b)	10.98	7.87	25.69	6.34	4.60	4.41	3.42	7.22
Sel to other								
Liquids	2.60	3.18	4.30	2.56	2.61	2.92	2.61	1.71

(a) See ex. 1 (b) BTX = benzene + toluene + xylenes.

(\*\*) See ex. 35; (\*\*\*) Na occupies 50% of the sites within the zeolite;

(\*\*\*\*) See ex. 11.

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TABLE 3

EXAMPLE	45	46	47	48	49	50	51	52
<b>Operative Conditions:</b>	(*)	(*)	(**)	(**)	(***)	(***)	(****)	(*****)
Catalyst	H-ZSM5	See ex. 45	See ex. 45	See ex. 45	See ex. 45	See ex. 49	H-ZSM5	See ex. 51
SiO <sub>2</sub> /Al <sub>2</sub> O <sub>3</sub> (moles)	28	"	"	"	28	"	28	"
Amount of catalyst	see ex. 23	"	"	"	see ex. 23	"	see ex. 23	"
Temp. (°C)	550	"	"	"	585	"	550	"
Space velocity (a)	71.4	"	"	"	178.5	214	71.4	357
Data survey after:	1 h	6 h	1 h	6 h	7 h	1 h	6 h	7 h
<b>Results (% b.v.)</b>								
Conversion	97.46	96.90	100	100	54.81	64.85	100	100
Selectivity to C <sub>2</sub> <sup>-</sup>	14.49	13.14	16.97	14.27	21.13	24.09	12.49	14.49
Selectivity to C <sub>3</sub> <sup>-</sup>	31.18	45.14	27.33	32.81	41.63	36.70	41.96	41.84
Yield (C <sub>2</sub> <sup>-</sup> + C <sub>3</sub> <sup>-</sup> )	44.51	56.47	44.30	47.08	34.40	39.42	54.45	56.33
Sel. to saturated compounds < C <sub>4</sub> <sup>-</sup>	6.54	2.12	6.00	2.93	1.97	3.72	1.86	1.01
Sel. to C <sub>4</sub> <sup>+</sup>	15.99	19.71	12.62	18.04	18.21	15.28	17.96	18.04
Sel. to C <sub>4</sub> <sup>+</sup> + C <sub>5</sub> <sup>+</sup>	5.84	1.43	7.13	4.02	1.53	3.19	1.28	0.58
Sel. to BTX (b)	11.81	3.42	16.13	10.83	10.29	13.26	6.97	6.14
Sel. to C <sub>5</sub> <sup>-</sup>	10.42	12.81	8.86	11.06	-	-	14.80	14.18
Sel. to others	3.68	2.26	5.13	5.67	5.20	3.90	2.68	3.72

(a) See ex. 1 (b) BTX = benzene + toluene + xylenes; (\*) Feed = n-hexene-1; (\*\*) Feed = n-octene-1; (\*\*\*) Feed = C<sub>5</sub> cut from F.C.C., containing C<sub>4</sub><sup>+</sup>, C<sub>5</sub><sup>-</sup> and dienes; (\*\*\*\*) Feed = 2-methyl-pentene + He; olefine/He = 0.7:1 by moles; (\*\*\*\*\*) Feed = pure 2-methyl-pentene, without He as diluent.

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TABLE 4

EXAMPLE	53	54	55	56	57	58	59	60
<b>Operative Conditions:</b>								
Catalyst	H-ZSM5	"	"	"	"	"	"	"
SiO <sub>2</sub> /Al <sub>2</sub> O <sub>3</sub> (moles)	28	"	"	"	"	"	"	"
Amount of catalyst	(b)	"	"	"	"	"	"	"
Temp. (°C)	597	"	550	"	500	"	450	"
Space velocity (a)	60	"	60	"	60	"	60	"
Data survey after:	1 h	5.30 h	1 h	4.30 h	1 h	4.30 h	1 h	6.15 h
<b>Results (% b.w.)</b>								
Conversion	92.4	91.6	91.2	85.5	92.0	82.6	91.6	90.0
Selectivity to C <sub>3</sub> <sup>-</sup>	24.2	32.2	22.0	26.2	14.0	18.4	12.0	13.0
Yield (C <sub>3</sub> <sup>-</sup> )	22.4	29.5	20.1	22.4	12.9	14.5	11.0	11.7
Sel. to C <sub>2</sub> <sup>-</sup>	6.74	8.46	4.95	2.96	2.35	1.84	1.64	1.33
Sel. to saturated compounds < C <sub>4</sub>	21.0	14.1	31.6	20.4	36.2	27.5	32.7	25.5
Sel. to compounds ≥ C <sub>5</sub>	32.9	30.6	22.4	21.0	27.5	30.1	35.1	39.7
Sel. to linear butenes	15.2	14.6	19.0	29.4	20.0	24.2	18.7	20.5

(a) See ex. 1; (b) See ex. 4.

T A B L E 4 (Continuation)

EXAMPLE	61	62	63	64	65	66	67	68
<u>Operative Conditions:</u>	(*)	(*)						
Catalyst	H-ZSM5	See ex. 61	See ex. 61	See ex. 63	See ex. 61	See ex. 65	See ex. 61	See ex. 67
SiO <sub>2</sub> /Al <sub>2</sub> O <sub>3</sub> (moles)	28	"	"	"	"	"	"	"
Amount of catalyst	(b)	"	"	"	"	"	"	"
Temp. (°C)	550	"	"	"	"	"	"	"
Space velocity (a)	470	"	296	"	216	"	136	"
Data survey after:	1 h	5 h	1 h	4 h	1 h	5.15 h	1 h	6 h
<u>Results (% b.w.)</u>								
Conversion	76.2	69.6	35.2	81.8	86.8	81.0	88.2	85.2
Selectivity to C <sub>3</sub> <sup>-</sup>	26.8	25.0	34.1	34.4	33.5	34.2	22.4	29.8
Yield (C <sub>3</sub> <sup>-</sup> )	20.4	17.4	29.1	28.1	29.1	27.7	19.8	25.4
Sel. to C <sub>2</sub>	1.61	1.30	4.92	3.81	5.49	3.48	2.85	3.64
Sel. to saturated compounds < C <sub>4</sub>	14.4	8.57	16.6	11.4	19.9	11.0	26.2	14.6
Sel. to compounds > C <sub>5</sub>	14.1	13.0	15.5	16.7	13.8	15.0	22.7	20.6
Sel. to linear butenes	43.1	52.0	28.8	33.7	27.4	36.2	25.8	31.4

(a) See ex. 1 (b) See ex. 4.

(\*) Comparative examples; space velocity is too high and either conversion or selectivity to C<sub>3</sub><sup>-</sup> decrease with the time.

TABLE 4 (Continuation)

EXAMPLE	69	70	71	72	73	74
<b>Operative Conditions:</b>						
Catalyst	H-ZSM5	See ex. 69	H-ZSM5	See ex. 71	H-ZSR5	See ex. 73
$\text{SiO}_2/\text{Al}_2\text{O}_3$ (moles)	28	"	204	"	28	"
Amount of catalyst	(b)	"	"	"	(b)	"
Temp. ( $^{\circ}\text{C}$ )	580	"	550	"	500	"
Space velocity (a)	216	"	60	"	60	"
Data survey after:	1 h	5.15 h	1 h	5.30 h	1 h	6.30 h
<b>Results (% b.w.)</b>						
Conversion	88.8	84.1	87.7	83.6	86.87	85.19
Selectivity to $\text{C}_3^-$	39.3	39.9	42.7	44.8	31.95	31.97
Yield ( $\text{C}_3^-$ )	34.9	33.6	37.5	37.4	27.76	27.24
Sel. to $\text{C}_2^-$	8.64	6.68	8.39	6.30	4.32	3.42
Sel. to saturated compounds $< \text{C}_4$	16.0	10.0	17.4	10.7	19.31	14.60
Sel. to compounds $\geq \text{C}_5$	15.0	15.4	10.2	10.4	20.31	23.33
Sel. to linear butenes	21.0	28.1	21.4	27.8	24.10	26.28

(a) See ex. 1; (b) See ex. 4.

(\*) Zeolite H-ZSM5 was activated 2 hours at  $700^{\circ}\text{C}$  before being used.

TABLE 4 (Continuation)

EXAMPLE	75	76	77	78	79	30	81
<u>Operative Conditions:</u>							
Catalyst	Cr-H-ZSM5	See ex. 75	Hg-H-ZSM5	See ex. 77	See ex. 77	H-ZSM5	See ex. 80
SiO <sub>2</sub> /Al <sub>2</sub> O <sub>3</sub> (moles)	28	"	See ex. 75	"	"	28	"
Amount of catalyst	(b)	"	"	"	"	(b)	"
Temp. (°C)	500	"	"	"	"	550	"
Space velocity (a)	80	"	"	"	"	3.5	"
Data survey after:	1 h	6 h	1 h	6.30 h	12 h	1 h	5.30 h
<u>Results (% b.w.)</u>							
Conversion	90.26	88.69	80.86	88.20	86.40	91.6	90.0
Selectivity to C <sub>3</sub> <sup>-</sup>	25.44	29.49	26.66	29.65	32.65	12.0	13.0
Yield (C <sub>3</sub> <sup>-</sup> )	22.96	26.15	23.98	26.15	28.21	11.0	11.7
Sel. to C <sub>2</sub> <sup>-</sup>	4.84	4.63	4.83	4.32	4.01	4.01	3.42
Sel. to saturated compounds < C <sub>4</sub>	25.50	17.78	26.72	18.94	15.88	46.0	37.3
Sel. to compounds ≥ C <sub>5</sub>	25.38	27.52	22.61	25.76	23.92	40.8	50.3
Sel. to linear butenes	18.83	20.58	19.18	21.34	23.54	3.0	3.0

(a) See ex. 1; (b) See ex. 4.

(\*) Comparative examples.

CLAIMS

1. A process for converting olefins having from 4 to 12 carbon atoms into propylene, characterised in that said olefins are contacted with an alumino-silicate having a crystalline and zeolitic structure and having a  $\text{SiO}_2/\text{Al}_2\text{O}_3$  molar ratio equal to or lower than 300, at a space velocity higher than 50 kg/h of olefins per kg of pure zeolite and at a temperature of from 400 to 600°C, whereby said alumino-silicate is preferably selected from zeolites ZSM 5 and ZSM 11, and is used as such or in a modified form.
2. The process of claim 1, wherein the crystallites of said alumino-silicates have an average size equal to or lower than 0.5  $\mu\text{m}$  and are selected from ZSM 5 and ZSM 11 zeolites, in which the  $\text{SiO}_2/\text{Al}_2\text{O}_3$  molar ratio is from 13 to 220, preferably from 25 to 220.
3. The process of claim 1 or 2, wherein the space velocity is from 60 to 300, preferably from 60 to 250  $\text{h}^{-1}$ .
4. The process of any of claims 1 to 3, wherein the zeolites are activated in air, before being used, at a temperature of from 450 to 750, preferably of from 540 to 700 °C.
5. The process of any of claims 1 to 4, wherein the zeolites are periodically regenerated with air at a temperature of from 400 to 600°C.
6. The process of any of claims 1 to 5, wherein the zeolites are admixed, before being used, with a binder, preferably selected from  $\text{SiO}_2$  and  $\text{Al}_2\text{O}_3$ .
7. The process of any of claims 1 to 6, wherein the zeolites are used in their acid form.



5 8. The process of any of claims 1 to 7, wherein said olefins are selected from isobutene, n-butenes and mixtures of olefins having 5 to 8 carbon atoms.

10 9. The process of any of claims 1 to 8, wherein the zeolites are used in a modified form with the modifying elements being selected from Mg, Ca, Sr, Ba, P, Cr, Cu, Zn and mixtures thereof.

15 10. A process for the conversion into propylene of mixtures of olefins having 4 C atoms, said mixtures containing also  $C_4^+$  paraffins that cannot be easily separated from olefins, which process comprises the following steps:

- 20 a) preliminary oligomerization of a  $(C_4^- + C_4^+)$  mixture at a temperature of from 320 to 380°C in a catalyst bed of zeolitic nature to obtain a mixture of olefins having from 5 to 8 C atoms, with the  $C_4^+$  paraffins remaining unconverted;
- 25 b) cooling and condensation of the oligomerization effluent in order to separate the  $C_4^+$  paraffins as a gaseous phase, and conversion of the remaining  $(C_5^- - C_8^-)$  mixture to propylene under the reaction conditions of claim 1;
- 30 c) cooling the effluent from the reactor for the conversion to propylene and compressing said effluent, preferably at 13 - 16 absolute kg/cm<sup>2</sup>, whereby the hydrocarbons having 4 or more C atoms are condensed and the hydrocarbons having less than 4 C atoms are separated as a gaseous phase.
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**FIGURE 1**



European Patent  
Office

# EUROPEAN SEARCH REPORT

0109059  
Application number

EP 83 11 1240

DOCUMENTS CONSIDERED TO BE RELEVANT			
Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int. Cl. 3)
A	EP-A-0 037 671 (MOBIL OIL CORP.) * Page 11, paragraph 2; page 17, paragraphs 1-2; claims *	1,2,4,6	C 07 C 11/06 C 07 C 4/10 B 01 J 29/28 B 01 J 29/38
A,D	--- EP-A-0 036 704 (MOBIL OIL CORP.) * Claims *	5	
A,D	--- US-A-4 150 062 (GARWOOD et al.) * Examples 5-6; claims * -----	10	
			TECHNICAL FIELDS SEARCHED (Int. Cl. 3)
			C 07 C 11/00 C 07 C 4/00
The present search report has been drawn up for all claims			
Place of search THE HAGUE		Date of completion of the search 30-01-1984	Examiner VAN GEYT J.J.A.
CATEGORY OF CITED DOCUMENTS			
X : particularly relevant if taken alone Y : particularly relevant if combined with another document of the same category A : technological background O : non-written disclosure P : intermediate document		T : theory or principle underlying the invention E : earlier patent document, but published on, or after the filing date D : document cited in the application L : document cited for other reasons & : member of the same patent family, corresponding document	